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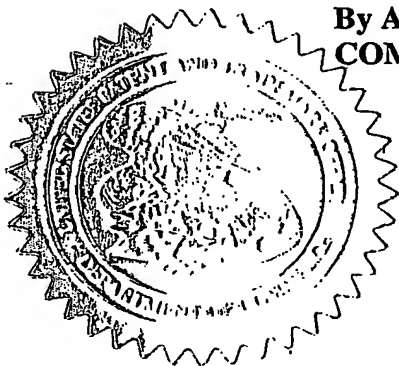
June 28, 2004

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APPLICATION NUMBER: 60/470,635

FILING DATE: May 15, 2003

RELATED PCT APPLICATION NUMBER: PCT/US04/15079



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COMMISSIONER OF PATENTS AND TRADEMARKS

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05-16-03

60470635 .05 15206

Docket No. 03-2-311

"Express Mail" mailing label number EV 237677696 US

Date of Deposit May 15, 2003

PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53 (c).

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TITLE OF INVENTION

A Method to Encapsulate Phosphor Via Chemical Vapor Deposition

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ENCLOSED APPLICATION PARTS

☒ Specification Number of Pages 11 including Drawings

METHOD OF PAYMENT

The Commissioner is hereby authorized to charge the Provisional filing fee of \$160.00 to Deposit Account Number 15-0685.

Was the invention made by an agency of the United States Government or under a contract with an agency of the United States Government?

☒ No ☐ Yes, the name of the U.S. Government agency and the Government contract number are: _____

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Fan et al.

Serial No. Herewith

Art Unit: Not Assigned

Filed: Herewith

Examiner: Not Assigned

For: A Method to Encapsulate Phosphor Via Chemical Vapor Deposition

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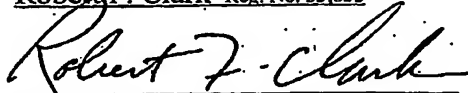
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A Method to Encapsulate Phosphor Via Chemical Vapor Deposition

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Technical Field

This invention relates to a method to encapsulate phosphor particles and more to encapsulate phosphor particles having a conformal coating there on. In particular, this invention relates to encapsulate plasma display (PDP) phosphor for protecting the phosphor particles from moisture attack, VUV radiation and Xe plasma bombardment thereby increasing the brightness maintenance.

Background

Conventional plasma display panels and other vacuum ultraviolet excited devices are filled with rare gases or mixtures of rare gases such as helium, neon, xenon, and krypton, which are excited by a high voltage electrical current and emit ultraviolet radiation in the VUV range below 200 nm wavelength. This emitted VUV radiation is then used to excite various blue, green, and red emitting phosphors. These phosphors differ from those typically used in conventional fluorescent lamps in that they are excited by high energy vacuum ultraviolet photons with wavelengths less than 200 nm while the conventional fluorescent lamp excitation energy is primarily the lower energy 254 nm emission from mercury vapor. Currently, the most common VUV excitation energy comes from xenon or xenon-helium plasmas, which emit in the region 147 nm to 173 nm, with the exact emission spectra depending on the Xe concentration and overall gas composition. Under high voltage excitation, Xe-based plasmas typically have a Xe emission line at 147 nm and a Xe eximer band emission around 173 nm.

The large difference in excitation energies between vacuum ultraviolet and conventional short-wave ultraviolet fluorescent applications impose new requirements on the phosphors used for VUV display panels or lamps. Furthermore, differences in the manufacturing processes used for VUV and conventional fluorescent devices also impose new requirements on the phosphors.

In general, the VUV excited phosphors used to emit all three colors (red, green, and blue), exhibit some undesirable properties, but the phosphor commonly used as the blue emitter, $\text{Ba}_{1-x}\text{Eu}_x\text{MgAl}_{10}\text{O}_{17}$ [$0.01 < x < 0.20$] or BAM, is most problematic. This phosphor is known to degrade in both brightness and color during the manufacturing process due to elevated temperatures and humidity. This phosphor also degrades in both brightness and color after extended exposure to the high intensity Xe plasma and VUV photon flux. Degradation mechanisms of BAM are the subject of much study and

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are thought to involve such changes as oxidation of Eu^{2+} to Eu^{3+} , modifications in the actual structure of the aluminate phosphor lattice, and movement of the Eu^{2+} activator ions between different sites within the lattice. The useful lifetime of a commercial plasma display panel is unacceptably short due to the shift in color point and intensity reduction of the blue phosphor component, which leads to an undesirable yellow shift in the overall panel color. The most relevant measure of this degradation is the maintenance of the intensity / CIE y color point. Both the intensity decrease due to degradation and the increase in CIE y color coordinate caused by a shift toward green in the color point result in a reduction of the I / y ratio.

In recent years, a number of different approaches have been attempted in order to improve the maintenance of blue VUV excited phosphors. These approaches include sol-gel coating of wide bandgap metal oxides onto BAM phosphor, thermal treatments of aluminate phosphors mixed with ammonium fluorides, solution based catena-polyphosphate coatings of BAM phosphor, substitution of alkali metals, alkaline earth metals, or zinc into the BAM stoichiometry, and preparation of a solid solution BAM-barium hexa-aluminate ($0.82\text{BaO} \cdot 6\text{Al}_2\text{O}_3$) phase, which exhibits improved color stability and maintenance but has an undesirable color point. Additionally, new phosphors with improved maintenance characteristics have been investigated such as $(\text{La}_{1-x-y}\text{zTm}_x\text{Li}_y\text{Sr}_z)\text{PO}_4$, $\text{Ba}_{1-a}\text{Eu}_a\text{MgAl}_6\text{O}_{11}$, $\text{CaMgSi}_2\text{O}_6\text{:Eu}^{2+}$; and $\text{CaAl}_2\text{O}_4\text{:Eu}^{2+}$.

Although many of these phosphors or phosphor complexes exhibit improvements in color and intensity stability, none have proven to be viable alternatives to the commercial standard blue VUV activated phosphor BAM. Thus, there is still a commercial need for improved blue VUV activated phosphors with reduced degradation characteristics. A desirable phosphor would have the following properties: a deeper blue color, improved color stability during panel manufacture, improved lifetime during panel operation, and a high relative percent maintenance of the intensity / CIE y color point after accelerated thermal, humidity, Xe plasma, and high intensity VUV photon flux testing.

SUMMARY OF THE INVENTION

Recently, we have found that europium activated calcium substituted barium hexa-aluminate, $\text{Ba}_{1.29-x-y}\text{Ca}_x\text{Eu}_y\text{Al}_{12}\text{O}_{19.29}$, [with $0 < x < 0.25$, $0.01 < y < 0.20$] previously described as a conventional fluorescent phosphor in U.S. Patent No. 4,827,187, and hereto forward described by the acronym CBAL, exhibits very desirable properties for use in VUV excited devices. This CBAL material has a deeper blue emission peak but with only 80 – 85% the initial intensity of a commercially available BAM blue VUV activated phosphor. Upon exposure to elevated temperature and humidity conditions, this material exhibits very nearly a zero shift in the color point and very little loss of intensity. Furthermore, upon exposure to a high intensity VUV photon flux used as an accelerated aging test, this material exhibits less than $\frac{1}{2}$ the intensity degradation found in a commercial BAM phosphor.

Furthermore, CBAL, europium-activated calcium-substituted barium hexa-aluminate, can be encapsulated by applying the new TMA/H₂O coating process while in a fluidized bed reactor resulting in significant additional improvements to its maintenance when exposed to the high intensity VUV photon flux. This material will be further described by the acronym cCBAL.

Laboratory tests have been designed to simulate actual PDP panel manufacturing and use which include a thermal humidity test and an accelerated aging test. Brightness before and after the thermal humidity and accelerated aging tests were obtained by measuring emission spectra using a Perkin-Elmer LS-50B spectrometer and quantifying them relative to the emission spectrum of a standard BAM phosphor reference. The peak wavelengths at maximum intensity were derived from the spectra and the y coordinate color values were calculated from the spectral data using well-known and accepted equations based on X, Y, Z – tristimulus curves. The excitation source is a commercially available xenon excimer lamp (XeCM-L from Resonance, Ltd., Barrie, Ontario, Canada) used to illuminate powder plaques while excluding air from the VUV beam path. The phosphor can also be mixed into a paste, coated onto alumina chips or "slides", and measured in this fashion.

The thermal humidity test involves exposing blue PDP phosphor samples to a warm water saturated air flow at 425 °C for 2 hours. The accelerated aging test involves exposure to a high intensity Xe plasma and VUV photon flux. The accelerated aging test is performed using a high-power rare-gas discharge "torture chamber," dubbed the VURAAC. The VURAAC consists of a 100 cm loop of 5 cm I.D. PyrexTM tube that has approximately 5 millitorr of flowing Xe after initially pumping down to a 10⁻⁶ torr vacuum. Other gases / combination of gases may also be used. An inductively coupled discharge is obtained after receiving approximately 280 watts of input power at 450 kHz from an RF power supply. It is estimated that there is approximately 90 milliwatts/cm² of 147 nm VUV radiation at the sample surface. No significant excimer emission is generated under these conditions. After a selected amount of time exposed to the Xe discharge, the samples were measured for brightness as described above.

Description of Invention

Many encapsulation methods, which employ the chemical vapor deposition in a fluid bed reactor have been disclosed to protect the phosphor particles from the moisture attack, VUV radiation and Xe plasma bombardment. However, the small-size (3 to 5 um of D50 size) PDP blue phosphors, such as BAM and CBAL are very difficult to fluidize which is due to their cohesive characteristics. Also, the Eu⁺² activator is very easy to oxidize under the oxidative environment. The method of this invention is a hydrolysis process which can be used to encapsulate the PDP phosphors. The gaseous water vapor is used not only to react with other reactant to form the coatings but also to help the fluidization of fine-size phosphor particles. Prior art hydrolysis encapsulation

processes have been practiced at a coating temperature of 200°C or below. However, by applying the hydrolysis of trimethyl aluminum process at 180°C on PDP phosphors, the coating didn't show any significant effect on protecting PDP phosphors from moisture attack. The deposited coating under the low temperature conditions is believed to be insufficiently dense enough to prevent the penetration of water molecules.

The new coating process applies the chemical vapor deposition technique to deposit a thin film of aluminum-containing compound on individual particles of phosphor powders. During the coating process, the particles were suspended in a fluidized bed and exposed to trimethyl aluminum precursor in an inert carrier gas at a bed temperature of 430°C or above. Also, the inert gas was passed through the heated water bubbler to carry the gaseous water vapor into the reactor. The gaseous water molecules then reacted with the trimethyl aluminum vapor to form a continuous coating on the surface of phosphor powders via the hydrolysis reaction of trimethyl aluminum. In this invention, it was found that the coating deposited on PDP phosphors under the high temperature conditions has significantly improved the humidity resistance. To demonstrate the effectiveness of coatings, several types of phosphor were encapsulated by applying this high-temperature hydrolysis coating process and then tested under various conditions..

Experimental Procedure

All the coating tests were conducted in a quartz tube with a 14 cm inside diameter and a length of 152 cm. For each run, a 4.0 kg quantity of phosphor was charged into reactor. An inert nitrogen flow of 15 liter per minute, which bypasses the TMA bubbler was first introduced into the bottom of the reactor to fluidize the phosphor particles. The phosphor particles were suspended by the nitrogen gas in the fluidized bed reactor and have the bed height of about 100 cm. The vibromixer was then turned on at a speed of 60 cycles/minute to help the circulation of phosphor particles inside the reactor. The fluidized bed reactor was heated and maintained at a temperature of approximately 430°C by means of an external furnace. Two thermocouples were placed inside the reactor to monitor the temperature profile of the bed. One located in the middle of bed was used to control the reactor temperature within $\pm 5^\circ\text{C}$ during the coating process. The other thermocouple is placed one inch above the distributor, which is located on the bottom of the reactor. When the reactor temperature approached to 430°C, a TMA pre-treatment step was initiated with nitrogen gas flowing through the trimethyl aluminum bubbler at 8.0 liter/minute. The TMA bubbler was kept at the temperature of 34°C and maintained the constant TMA vapor pressure. The second nitrogen gas stream containing the vaporized trimethyl aluminum precursor was mixed with the 15.0 liter/minute nitrogen gas stream which bypassed the TMA bubbler and flowed into the base of the fluidized bed reactor. This dilute trimethyl aluminum precursor vapor passed through a metal frit distributor located under the tube reactor and used to support the phosphor particle bed. After the surfaces of phosphor powders were saturated with TMA precursor for one minute, the gaseous water vapor was transported into the reactor via a third stream of nitrogen gas with the flow rate of 14 liter/minute. This nitrogen

stream was passed through a water-filled bubbler which is maintained at the temperature of 70°C. The water vapor and nitrogen mixture was flowed into the reactor through a series of fine holes circumferentially located on the hollow shaft of vibromixer above the vibrating disc to start the coating process. The coating reaction was allowed to proceed until the desired quantity of hydrolyzed TMA coating has been produced. The final product was collected at the end of coating experiment for chemical analyses, environmental tests and brightness measurement.

Example 1.

CBAL can be made by thoroughly blending aluminum hydroxide, barium carbonate, calcium carbonate, europium oxide, and barium fluoride and then firing the resulting mixture in alumina-based trays for between 2 and 4 hours in a reducing furnace under a nitrogen-hydrogen atmosphere (ranging from 5% hydrogen to 75% hydrogen with the remainder being nitrogen gas) at temperatures from 1400°C to 1600 °C. The fired cakes are washed in de-ionized water and wet sieved through a 378 mesh screen or alternatively lightly milled before wet sieving 378 mesh. The material is dried and dry screened through a 60 mesh sieve to break up any possible agglomerates. One non-limiting example of a CBAL formulation is listed below.

CBAL Formulation

Reagent	molar ratio	wt. Ratio (adjusted by assay)
Al(OH)₃	11.0000	6.9076
CaCO₃	0.1700	0.1366
BaF₂	0.1000	0.1407
Eu₂O₃	0.0400	0.1153
BaCO₃	0.8325	1.3251

Results

Samples of CBAL(lot no. 4) and high-temperature hydrolyzed TMA coated cCBAL were prepared, their emission spectra collected, and then subjected to degradation testing as described above. It is thought that these accelerated degradation tests closely mimic conditions found in PDP panel manufacture and use. Furthermore, it is thought that the results are relevant for comparison with the degradation found during manufacture and use of any VUV excited device. The application of high-temperature hydrolyzed TMA coating significantly improves the maintenance characteristics of CBAL phosphor. Results from these tests are listed below in Table 1.

Table 1. Optical Emission Results from Initial and Degraded Blue VUV Excited Phosphors [TH = degraded due to elevated temperature and humidity; X = degraded by high intensity Xe plasma and VUV photon flux; THX = degraded due to elevated

temperature and humidity followed by high intensity Xe plasma and VUV photon flux] /
Intensity is Measured Relative to a Standard Blue PDP BAM Phosphor.

	Powder Plaque Data			Paste Slide Data		
	BAM control	Uncoated CBAL	Coated cCBAL	BAM control	Uncoated CBAL	Coated cCBAL
Intensity (initial)	96%	76%	68%	104%	84%	79%
Peak λ (initial)	446 nm	439 nm	439 nm	446 nm	439 nm	439 nm
Initial y value	0.0465	0.0568	0.0553	0.0466	0.0518	0.0517
Intensity (TH)	87%	74%	69%	96%	82%	79%
Peak λ (TH)	456 nm	439 nm	439 nm	456 nm	439 nm	439 nm
(TH) y value	0.0803	0.0571	0.0566	0.0771	0.0527	0.0542
% I / y (TH)	52%	96%	98%	56%	96%	95%
Intensity (X)	57%	42%	49%	76%	61%	66%
Peak λ (X)	446 nm	439 nm	439 nm	446 nm	439 nm	439 nm
(X) y value	0.0527	0.0625	0.0608	0.0504	0.0565	0.0563
% I / y (X)	53%	50%	65%	68%	66%	76%
Intensity (THX)	52%	47%	49%	64%	60%	65%
Peak λ (THX)	454 nm	439 nm	439 nm	454 nm	439 nm	439 nm
(THX) y value	0.0901	0.0642	0.0633	0.0905	0.0596	0.0602
% I / y (THX)	28%	54%	63%	32%	62%	70%

The degradation results from powder and paste samples are basically equivalent. Although the paste brightness results tend to be higher than the powder brightness values, they are relatively the same. The peak wavelength at maximum intensity does not change for either the CBAL or cCBAL samples while the BAM control sample shows a large shift in color after the thermal humidity test. The initial brightness for the BAM control is much higher than the initial brightness of the CBAL and cCBAL samples, while after exposure to the thermal humidity test and the high intensity Xe plasma and VUV photon flux, all samples have comparable brightness. The maintenance of % I / y (Intensity / y) for the CBAL sample after (THX) thermal humidity and Xe plasma testing is vastly superior to that of the BAM control [54% vs. 28% and 62% vs. 32%] and the maintenance of coated CBAL (cCBAL) is further superior to that of uncoated CBAL [63% vs. 54% and 70% vs. 62%]. The coated cCBAL material also exhibits significantly improved maintenance after high intensity Xe plasma and VUV photon flux exposure without any thermal humidity tests being involved.

Example 2.

The manganese-activated zinc silicate ($\text{Zn}_2\text{SiO}_4\text{:Mn}$) is an efficient green emitting phosphor for plasma display panels, and it also presents the advantage of having a high saturated color. This phosphor is very stable during the PDP panel manufacturing process at the elevated temperature and humidity. No significant brightness degradation and color shift were observed. However, the degradation of phosphor brightness is significant under the ion bombardment and VUV radiation. To improve the brightness maintenance of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphor, Sylvania type 9310 (lot no. TGX34) green phosphor was used to conduct the coating experiments. For comparing the effectiveness of hydrolyzed TMA coatings under the accelerated aging (VURAAC) test, phosphor powders were encapsulated by using the hydrolysis TMA coating process at both low (180°C) and high (430°C) temperature. The uncoated and coated phosphors were mixed with paste and then conducted the binder burn out (BBO) and VURAAC tests. The initial brightness (after BBO test), final brightness (after VURAAC test) and the maintenance (ratio of final brightness/initial brightness) were measured and listed in the table 2.

Table 2. The effect of hydrolyzed TMA coating on brightness maintenance of PDP green phosphor.

Sample	Initial Brightness, %	Final Brightness, %	Maintenance, %
Uncoated	100	74.8	74.8
Coated at 180°C	84.8	62.8	74.0
Coated at 430°C	80.7	69.5	86.0

Based on the data shown in table 2, no enhancement of brightness maintenance was observed when the phosphor was encapsulated by using the hydrolysis reaction of TMA at 180°C. However, the brightness maintenance was improved significantly from 74.8% to 86.0% when the hydrolyzed TMA coating was deposited on phosphor surface at the temperature of 430°C.

Example 3.

Lead-activated barium disilicate ($\text{BaSi}_2\text{O}_5:\text{Pb}$) is used as the long-wavelength UV (347 nm) phosphor in fluorescent suntanning lamps. A well-known drawback to the use of this phosphor is that lumen maintenance in fluorescent lamps is poor relative to other fluorescent lamp phosphors. It has been demonstrated generally that the maintenance of this phosphor can be improved by applying a protective alumina coating via the chemical vapor deposition method. Phosphor particles are typically encapsulated by reacting oxygen with trimethyl aluminum vapor at the temperature of 430°C or above. The coated phosphor then need to be annealed at about 800°C to remove the residual carbon from the incompletely reacted TMA deposited on phosphor and also bond the coating into the particle surface. After the annealing, the body color of phosphor powder change from slightly brownish appearance to white. Also, the powder brightness improves from about 80% to 100% verse the control sample. It would be more economical for using water vapor instead of pure oxygen to form the protective coating on silicate phosphors.

One batch of Sylvania type 2011C ($\text{BaSi}_2\text{O}_5:\text{Pb}$) phosphor was encapsulated well by applying the coating method of hydrolysis of trimethyl aluminum at the temperature of 180°C. However, the low-temperature hydrolyzed TMA coated phosphor didn't turn white but showed the grayish color after the sample being annealed at 800°C. The brightness of these phosphors was measured under UV excitation (254 nm) and is compared in table 3.

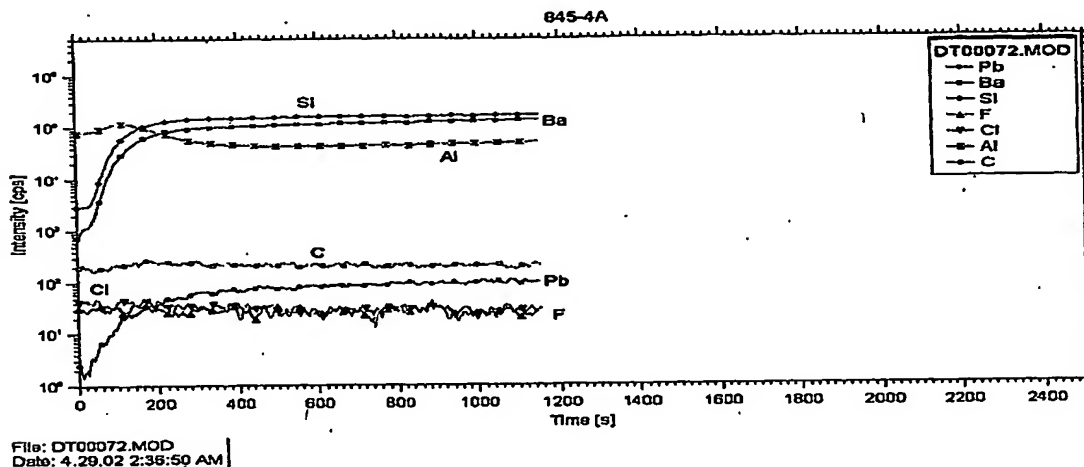
Table 3. Comparison between oxidized TMA coating and hydrolyzed TMA coating processes.

Sample Description	Relative Brightness (coated only), %	Relative Brightness (coated and annealed), %
Oxidized TMA	80.5	102.4
Hydrolyzed TMA at 180°C	82.0	79.6
Hydrolyzed TMA at 430°C	77.3	101.5

By comparing the brightness data, the oxidized TMA coated and annealed product outperformed the low-temperature hydrolyzed TMA coated and annealed sample by

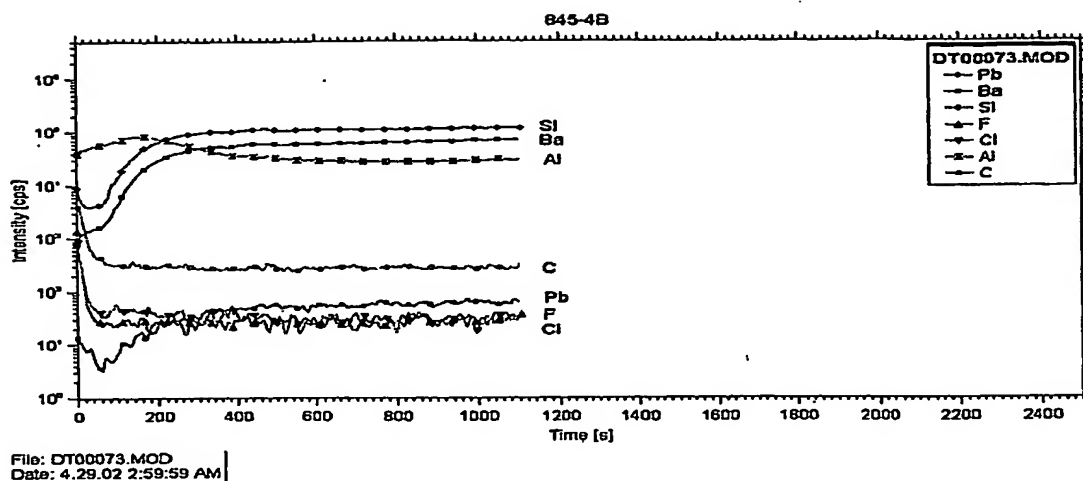
more than 22% (102.4% vs. 79.6%). Since there is no surface Pb being detected on both samples by using the ESCA, the SNMS analysis was used to explore the possible diffusion underneath of the particle surface. The following graphs on figure 1 showed the element depth profile of low-temperature hydrolyzed TMA coated but before annealed sample.

Figure1. The SNMS depth profile of low-temperature hydrolyzed TMA coated sample.



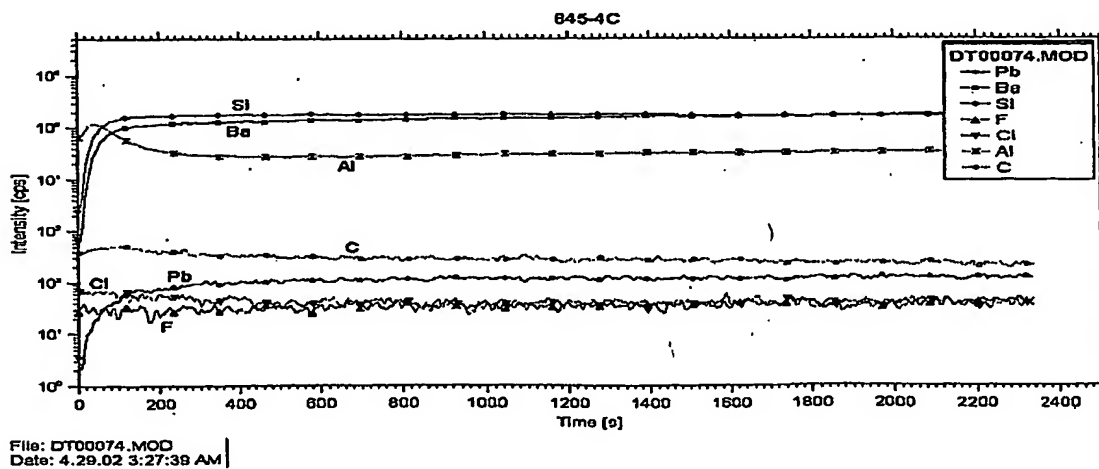
The Al profile clearly indicated the aluminum type coating is on the surface of low-temperature hydrolyzed TMA coated particles. The next graph of figure 2 showed the element depth profile after the low-temperature hydrolyzed TMA coated phosphor being annealed at 800°C.

Figure 2. The SNMS depth profile of low-temperature hydrolyzed TMA coated and annealed sample.



Based on this graph, almost all the elements including Si, Pb, C, F, and Cl showed some degrees of diffusion from bulk structure to the surface after the annealing step. For the comparison purpose, the next graph of figure 3 was obtained from the oxidized TMA coated and annealed sample.

Figure 3. The SNMS depth profile of oxidized TMA coated and annealed sample.



There is no sign of Pb or any other element diffusion to the surface for the oxidized TMA coated sample. From all these results, it appears that the coating produced from the hydrolyzed TMA process at 180°C may be more porous than the coating generated from the oxidized TMA coating at 430°C. During the annealing treatment on the low-temperature hydrolyzed TMA coated sample, the elements such as Pb diffused from the silicate bulk structure through the coating layer and exhibited the body color resulting to low brightness. However, if the hydrolyzed TMA coating process was conducted at 430°C instead of 180°C, coating deposits appear less porous and can minimize the diffusion of Pb to the surface. The following SNMS graph of figure 4 confirms that there is very little Pb diffusion through the high-temperature hydrolyzed TMA coating. This is why the brightness of annealed product is measured as 101.5%.

Figure 4. The SNMS depth profile of high-temperature hydrolyzed TMA coated and annealed sample.

